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COUNTRY USSR/Rumania

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SUBJECT Polyethylene

Re: research connected with above

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Low Pressure Polymerisation of Ethylene

A new approach to the low pressure polymerisation of ethylene has been foreshadowed in a recent note from Professor Nenitzescu and co-workers of the organic chemistry department of the RVR Academy in Bucharest, published in "Angewandte Chemie," 1956, 68, 438. This work is as yet in a very early stage and it is not possible to say what its industrial implication may be. There is no doubt that further announcements from Professor Nenitzescu's laboratory will be awaited with interest in view of the possibility of a route to polythene, apparently independent of existing patents.

AMONG the simple olefines ethylene has the least tendency to polymerise and the older processes for polymerisation of ethylene, which is used on the production scale, requires pressures between 1,000 and 2,000 atmospheres and a temperature of about 200° C. For this reason the observation of K. Ziegler and his associates that ethylene may be polymerised at normal pressures and lower temperatures by use of aluminium alkyls is the most significant discovery which has emerged in the field of macromolecular chemistry during the last two decades.

It appeared interesting, from the theoretical standpoint, to determine the part played by the titanium tetrachloride used by Ziegler and his collaborators as an activator or co-catalyst. It seemed reasonable to suppose that an exchange reaction of the type well-known among organo-magnesium compounds took place between the aluminium alkyl and the titanium tetrachloride, with formation of an organo-titanium compound. This reaction may be formulated as follows (RAl = equivalent of aluminium alkyl):—

$$nRAl + TiCl_4 \rightarrow R_nTiCl_{(4-n)} + nAlCl \quad (n \leq 4)$$

If this hypothesis were valid, then the true promotor of polymerisation would be the organo-titanium compound and the sole function of the aluminium alkyl would be to supply the alkyl radicals necessary to the formation of the titanium complex. The aluminium alkyl should then be replaceable by other reactive metallo-organic compounds. It would be the presence of a titanium compound which was essential to the polymerisation process.

In order to test this hypothesis, zinc diethyl, phenylsodium and isoamylsodium were used in that order. In all three cases a solid polythene resulted. Isoamylsodium appears to be the most efficient catalyst, though the other two alkyls were only slightly inferior. The procedure* in the preliminary investigation was as follows:

The solvent used was a petroleum fraction with a boiling range of 150-200° C. By conventional procedure, sodium under nitrogen was finely divided in a sulphonation flask equipped with an efficient stirrer. Isoamyl chloride at a temperature of - 10° was added drop by drop and cooling applied until the heat developed had dispersed. Titanium tetrachloride dissolved in the same solvent was then added slowly at about 20° C. The resulting solution was transferred to the polymerisation vessel and thinned with solvent to a volume of about 400 ml.; ethylene was then introduced. The speed at which ethylene is absorbed, itself great, is very dependent upon the efficiency of stirring. The temperature rises rapidly and is maintained by external cooling at 70° C.

In the experiments so far carried out, 0.5 g. of sodium (with other reagents in equivalent quantities) was used in 400 ml. of solvent; 12.5 g. of polythene were produced. The abatement in ethylene absorption towards the end of the reaction appears to be due to the highly viscous state of the reaction mass—which prevents effective stirring—rather than to decreased efficiency of the promotor. The polymerisation product was treated by addition of alcohol, followed by washing with weakly acid water and drying. The polythene obtained was a light, white, easily filterable powder.

It is not yet possible to decide whether the mechanism of the reaction is of a radical or anionic nature. In the first case, it would be presumed that free radicals and a compound of trivalent titanium would be formed by thermal decomposition of the unstable titanium compound:—

$$R \cdot TiX_4 \rightarrow R \cdot + TiX_3$$

$$R \cdot + CH_2 = CH_2 \rightarrow R \cdot CH_2 - CH_2 \cdot \text{ etc.}$$

An anionic mechanism is thought to be less probable.

The detection of trivalent titanium would be an argument for the radical mechanism.

VIEWPOINT

Activators

IN OUR ISSUE of 21 July, 1956 (p. 107) we published a note by Professor Nenitzescu *et al.*, of Bucharest, about the use of zinc and sodium alkyls as activators for titanium tetrachloride in the normal pressure polymerisation of ethylene. The main point made in the work was that the true polymerisation catalyst in the process first described by Professor Ziegler was an organo-titanium complex, and the aluminium alkyl was almost incidental, serving only as a source of alkyl radicals

Professor K. Ziegler in a recent note in *Angewandte Chemie* (1) has now pointed out that the Rumanian work is already anticipated to some extent by previous and current work by his own Institute. His comments are as follows:

'In the article "The Mulheim Normal Pressure Ethylene Process" which I published in this journal (2) together with E. Holzkamp, H. Breil and H. Martin not quite a year ago, after the paper had been read on 14 September in Munich, there appears on page 547 in paragraph 4 of the left-hand column, the sentence "the fact that titanium tetrachloride in particular can be transformed to polymerisation activating material with other types of reducing agents, without use of aluminium or other metal alkyls, was shown by Herr Breil in the course of his Diploma and Doctorate theses."

'On the same page, in paragraph 2 of the right-hand column, there appears, during a discussion on a British Patent of Du Pont, the sentence: "It is curious that this patent names all the heavy metals, such as Ti, Cr, V, whose compounds in combination with the same alkyl compounds of the alkaline metals, magnesium or zinc, give excellent catalysts for the process which we have discovered. It is only that the metals have been recommended for the wrong purpose, i.e. the activation of redox systems!" The sense of these sentences could hardly be misunderstood.

'It is clear from them that alkyl compounds of metals other than aluminium form with titanium tetrachloride (also of course with compounds of other heavy metals) polymerisation catalysts for ethylene. The use of zinc alkyls (and organic magnesium compounds) is described in my Belgian Patent No. 534,888 and that of alkali metal alkyls in my Belgian Patent No. 543,913.

'The state of our knowledge regarding metal alkyls in spring 1954 is summarised by Breil (3) in his diploma thesis in the following general rule:

"If one mixes organic compounds of the metals lithium, sodium (potassium, rubidium, caesium?), (beryllium?), magnesium (calcium, strontium, barium?), zinc (cadmium, mercury?), aluminium (gallium, indium?), with compounds of metals of the fourth, fifth and sixth sub-groups of the periodic system, then one obtains more or less highly active 'metallo organic mixed catalysts' for the polymerisation of ethylene."

'Set in brackets and marked with question marks are those metals upon the organic compounds of which no direct experiment had been made at that time (during 1954).

'My Institute must at present exercise restraint on the publication of its work in detail. However, anybody stimulated by our first publication to work in this field, can easily find himself in already anticipated territory. This has occurred in the case of the Rumanian workers (4).

'Finally it may be said that of course we have not left uninvestigated the problems of the nature of catalysts and the mechanism of formation of polythene. The black material which, in the limiting case, is ultimately formed from $TiCl_4$ and metal alkyls of the above type when there is suitable excess of the alkyl contains $Ti^{II}:Ti^{III}$ in proportion 1:1. The whole problem of the new catalysts is not, however, exhausted by this observation.'

REFERENCES

(1) *Angew. Chem.*, 1956, **68**, 581.
(2) *Ibid.*, 1955, **67**, 541.
(3) Submitted in June 1954 at Bonn University.
(4) *Angew. Chem.*, 1956, **68**, 438.

OUR NEW SIZE

WITH this issue THE CHEMICAL AGE appears in large size, having been a pocket size publication since 4 July 1942. The publishers have devoted much thought to the design and layout of the new size and the paper now appears as an example of the best in contemporary typographical practice.

The spacious format and large type make for ease of reading, while diagrams and illustrations can now be reproduced in a size which will ensure clarity. The publishers believe that the new size will give added prestige to THE CHEMICAL AGE and that this will, in turn, reflect credit on the British chemical industry in the 64 countries where the paper circulates. Readers will notice that the change in size has involved a change in volume number. Thus, the issues for July, August and September will comprise Vol. LXXV, an index for which will be available in due course. This large size issue is the first of Vol. LXXVI.